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(54) Method of removing soot from lubricating oils.

(57) Soot can be effectively removed from a lubricating oil used in a non-gasoline fueled internal combustion engine by contacting the oil with a heterogenous strong base. This results in improved engine cleanliness and reduced engine wear.

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alumina weight. The difference in weight is expressed as grams of water per dram of dry alumina. A saturated solution of calcium hydroxide in water is prepared. This solution is then added to the dry alumina in an amount equal to the difference between the weight of wet and dry alumina. The water is removed from the alumina with heat leaving $\text{Ca}(\text{OH})_2$ deposited on the alumina as the product. This preparation can be carried out at ambient conditions, except the water removal step is performed above 100°C .

Once the soot has been removed from the oil, the deposits thus formed will be immobilized as heterogenous deposits with the strong base or with the strong base on a substrate if one is used. Thus, soot which would normally remain dispersed in the oil is removed therefrom as deposits.

Soot may be present in essentially any lubricating oil used in the lubrication system of essentially any non-gasoline fueled internal combustion engine. Thus, as used herein, "internal combustion engine", refers to essentially any internal combustion engine except those that are gasoline fueled. This includes non-gasoline fueled automobile and truck engines, two-cycle engines, aviation piston engines, marine and railroad engines, gas-fired engines, alcohol (e.g., methanol) powered engines, stationary powered engines, turbines, and the like. However, soot is primarily a problem in compression ignition engines such as diesel engines, especially modern design diesel engines with high fuel injection pressure. The trend in diesel engine design of increasing the fuel injection pressure to produce smaller fuel droplet size will likely exacerbate the problem because, although smaller fuel droplet size produces less particulate emissions, the formation of soot in lubricating oil is often increased.

In addition to soot, the lubricating oil will normally comprise a major amount of lubricating oil basestock (or lubricating base oil), and a minor amount of one or more additives. The lubricating oil basestock can be derived from natural lubricating oils, synthetic lubricating oils, or mixtures thereof. In general, the lubricating oil basestock will have a viscosity in the range of about 5 to about 10,000 cSt at 40°C , although typical applications will require an oil having a viscosity ranging from about 10 to about 1,000 cSt at 40°C .

Natural lubricating oils include animal oils, vegetable oils (e.g., castor oil and lard oil), petroleum oils, mineral oils, and oils derived from coal or shale.

Synthetic oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymers of olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes), etc., and mixtures thereof); alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzene, etc.); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls, etc.); alkylated diphenyl ethers, alkylated diphenyl sulfides, as well as their derivatives, analogs, and homologs thereof; and the like.

Synthetic lubricating oils also include alkylene oxide polymers, interpolymers, copolymers and derivatives thereof wherein the terminal hydroxyl groups have been modified by esterification, etherification, etc. This class of synthetic oils is exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide; the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl-polyisopropylene glycol ether having an average molecular weight of 1000, diphenyl ether of polyethylene glycol having a molecular weight of 500-1000, diethyl ether of polypropylene glycol having a molecular weight of 1000-1500); and mono- and poly-carboxylic esters thereof (e.g., the acetic acid esters, mixed C_3 - C_8 fatty acid esters, and C_{13} oxo acid diester of tetraethylene glycol).

Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol, etc.). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid, and the like.

Esters useful as synthetic oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, triptaerythritol, and the like. Synthetic hydrocarbon oils are also obtained from hydrogenated oligomers of normal olefins.

Silicon-based oils (such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils) comprise another useful class of synthetic lubricating oils. These oils include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-2-ethylhexyl) silicate, tetra(p-tert-butylphenyl) silicate, hexa-(4-methyl-2-pentoxyl)-disiloxane, poly(methyl)-siloxanes and poly(methylphenyl) siloxanes, and the like. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid), polymeric

Thus, this invention can be combined with removing PNA's from a lubricating oil, enhancing the performance of a lubricating oil by releasing conventional additives into the oil, or to both. In these embodiments, the substrate (if one is used) and sorbent may comprise the same material.

Although this invention has heretofore been described with specific reference to lubricating oils used in non-gasoline fueled internal combustion engines, it can also be suitably applied to essentially any oil (e.g. industrial lubricating oils) that contains soot.

This invention may be further understood by reference to the following examples which are not intended to restrict the scope of the appended claims. In these examples, the amount of soot in an oil sample was determined by thermal gravimetric analysis (TGA). TGA is an analytical technique in which an oil sample suspended on an arm of a thermobalance is heated and held within the constant temperature zone of a furnace through which a controlled atmosphere is passed. The loss or gain in sample weight is measured as a function of a temperature program applied to the furnace. The composition of the gas flowing through the furnace can be changed during the test run. A TGA procedure has been described by McGeehan and Fontana (Effect of Soot on Piston Deposits and Crankcase Oils - Infrared Spectrometric Technique for Analyzing Soot, SAE paper, 801368, 1981). Another TGA method is described in ASTM E1131, Standard Test Method for Compositional Analysis by Thermogravimetry.

However, the particular TGA procedure employed in the examples below uses temperature and gas profiles that differ from those in the above two references as follows: the temperature was raised from 25 °C (room temperature) to 600 °C at a rate of 20 °C/minute in an N₂ atmosphere; at 600 °C the atmosphere was switched to air and the temperature held for 5 minutes; and the temperature was then raised to 680 °C at a rate of 20 °C/minute. All the weight loss after air replaced N₂ is considered as fixed carbon. As used herein, soot refers to the amount of pyrolyzable hydrocarbon and fixed carbon.

25 Example 1 - Soot Removal Using NaOH on Carbon

Used oil from a Mack T7 engine test was used to demonstrate the ability of a strong base to reduce the viscosity of the used oil by removing soot from the oil. The viscosity of the used oil before treatment with strong base was 26.6 centistokes at 100 °C and 257.5 centistokes at 40 °C. In this example, 2,000 grams of used oil was circulated at a rate of 2,000 ml/min through a filter containing 170 grams of NaOH on an activated carbon substrate. After 8 hours the viscosity of the oil was 17.7 centistokes at 100 °C and 145.6 centistokes at 40 °C. Using the modified TGA procedure described above, the amount of soot in the oil before and after contact with the NaOH on carbon was measured to be 20.6% and 10.7%, respectively, which corresponds to a 48.1% reduction in soot. The results obtained from this example are summarized in Table 1 below.

Example 2 - Soot Removal Using ZnO on Alumina

2,000 grams of the used Mack T7 oil from Example 1 was circulated at a rate of 2,000 ml/min through a filter containing 192 grams of ZnO on an alumina substrate. After 8 hours the viscosity of the oil was 22.3 centistokes at 100 °C and 149.0 centistokes at 40 °C. The amount of soot before and after contact with the ZnO on alumina was 20.5% and 9.4%, respectively, which corresponds to a 54.1% reduction in soot. The results obtained from this example are also summarized in Table 1 below.

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16. The method of claim 15 wherein the lubricating oil additive is an antiwear agent, an antioxidant or a friction modifier, or mixtures thereof.

17. The method of any preceding claim wherein the internal combustion engine is a diesel engine.

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